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Thermodynamic properties of aluminium (Al) at high temperatures and high pressures using local pseudopotential with mean-field potential approach : a comparative study

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Abstract : A conjunction scheme is used for calculating several thermodynamic properties, such as equation of states (static compression as well as shock-Hugoniot), relative volume-thermal expansion, bulk moduli (B_T and B_S), internal energy, specific heats (C_V and C_P), anharmonic ionic contribution to the specific heat (C_V^{anh}), thermodynamic Grüneisen parameter (γ_{th}), Hugoniot temperatures and high-pressure melting curve for elemental fcc-Al. We couple, alternatively, local pseudopotential due to Fiolhais *et al* [*Phys. Rev.* **B51** 14001 (1995)] to recently proposed mean-field potential (MFP) approach by Wang and Li [*Phys. Rev.* **B62** 196 (2000)] to account for the vibrational contribution of the lattice ions. Results are satisfactorily compared with the *ab initio* calculations and with the experiments.

Keywords : Mean-field potential, pseudopotential, thermodynamic properties

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1. Introduction

The study of thermodynamic properties of materials at high temperatures and high pressures is essential in many fields of basic and applied sciences including geophysics and astrophysics. Any study of the temperature dependence of material properties requires a proper description of nuclear motions and thermal excitation of electrons. Within the density-functional framework, the latter contribution can be taken into account by using the Mermin functional [1] rather than conventional density-functional theory (DFT). The treatment of ion-motional to the total Helmholtz free energy on an equal footing is less straightforward. Though, with increasingly powerful computers and efficient algorithms, highly accurate *ab initio* or first principle methods [2–9] are used nowadays to determine thermal properties; some alternative simpler approaches have also been attempted [10–14].

As for temperature dependence properties study, mean-field approximation, ever since its introduction [15], remains a subject of preference for the theoretical physicist, due largely to its simplicity and competence of producing results which are consistent with the experimental data. With different physical points of view, various mean-field approximations have been proposed in literature [2,3,16–19]. Since for a crystal with inversion symmetry, lattice vibration is symmetrical with respect to equilibrium position, and therefore, mean-field potential (MFP) seen by the lattice ion should also be invariant. Based on this physical argument, recently, Wang and Li [2] have proposed a simple means of calculating MFP in terms of 0-K total energy E_C and this has allowed the vibrational free energy (F_{ion}) to be calculated by solving only one-dimensional numerical integration. The only requirement (since the free energy due to thermally excited electrons is usually

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diminutive) in this approach is the precise determination of 0–K total energy-volume relation, which these authors have obtained employing full-potential linearized augmented plane wave (FP-LAPW) method within the generalized gradient approximation (GGA), while the free energy due to thermally excited electrons was calculated through electronic density of states (DOS) Further, they have developed an *ab initio* scheme for evaluating thermodynamic properties of material at an extreme environment An *ab initio* MFP approach when applied to elemental metals namely, Al, Cu, Ta, Mo, W, and also *f* shell metals Th, Ce and U, resulting 300 K isotherm and shock Hugoniot were found in excellent agreement with the experimental results. Wang [16] found that isostructural γ-α phase transition can naturally be observed with this approach The calculations on metallic Al [2] are the best manifestation of the ability of the MFP to illustrate correctly most of the thermodynamic properties at high pressures and high temperatures These reflect the reliability of first principles methods, but they are relatively lengthy and intricate.

On the other hand, empirical pseudopotential perturbation theory has possibly been the versatile tool in studying several physical properties of simple metals [20], and appropriate refinements have made it possible to treat less simple metals on the same merits [21–23] Fiolhais *et al* [24] have proposed 'structured stabilized jellium' model pseudopotential, so called 'evanescent' pseudopotential, and tested its reliability against sixteen metals including empty *d*-band prototype metals namely, Ca, Sr and Ba They have calculated binding energies, bulk moduli and their pressure derivatives at 0–K and at zero-pressure, and have noted that bulk equilibrium properties of some metals are in better agreement than that attained by first principles nonlocal norm-conserving pseudopotentials. Katsnelson *et al* [25] and Godwal *et al* [26] have shown that the computed equation of state and shock Hugoniot for simple metals using reliable local pseudopotentials are very close to the first principles calculations

Encouraged by the aforesaid facts, we in the present communication, intend to observe the applicability of the local pseudopotential in conjunction with the MFP approach due to Wang and Li [2] We have coupled local pseudopotential due to Fiolhais *et al* [24] (to calculate 0 K total energy) with the MFP approach. In this paper, we carry out a comparative study for thermodynamic properties of Al with the stated coupling scheme, which has an added benefit of simplicity offered by the local pseudopotential formalism. Our aim is to compare the results so generated with the experiments and those due to sophisticated first principles calculations, and also to examine the transferability and reliability of the local pseudopotential used in an extreme environment, such as high-temperature and high-pressure

The paper is organized as follows In Section 2, we present some details about the construction of the MFP and the pseudopotential used to construct the MFP The relevant expressions for computing the thermophysical properties are described in Section 3 The computed results are compared with experimental and available theoretical results in Section 4 The paper is summarized and concluded in Section 5

2. Mean-field potential approach

For a substance, if we have the Helmholtz free energy as an explicit function of volume and temperature, we can calculate all other thermodynamic properties The Helmholtz free energy $F(\Omega,T)$ per ion can be written as,

$$F(\Omega,T) = E_C(\Omega) + F_{ion}(\Omega,T) + F_{eg}(\Omega,T) \qquad (1)$$

Here, E_C represents the static total energy at 0 K, F_{ion} the vibrational free energy of the lattice ions and F_{eg} the free energy due to thermal excitation of the electrons

The static 0–K total energy E_C in eq (1) is calculated within the framework of pseudopotential theory Based on second order pseudopotential theory, E_C can be written as

$$E_C = Z(e_k + e_x + e_c) + E_{es} + E_p + E_{bs} \qquad (2)$$

First term of above equation, $Z(e_k + e_x + e_c)$, is known as uniform electron gas energy Here, e_k, e_x and e_c represent the kinetic, exchange and correlation energies of the homogeneous electron gas of charge Z. The second term is the electrostatic energy E_p and E_{bs} are the first and second order band structure energies, respectively. We have used local pseudopotentials proposed by Fiolhais *et al* [24], which has the following form in q-space

$$\omega_b(q) = \left(\frac{8\pi Z R^2}{\Omega}\right)\left[\frac{-1}{(qR)^2} + \frac{1}{\left[(qR)^2 + \alpha^2\right]} + \frac{2\alpha\beta}{\left[(qR)^2 + \alpha^2\right]^2} + \frac{2A}{\left[(qR)^2 + 1\right]^2}\right], \qquad (3)$$

where parameters A and β are expressed in terms of α as

$$\beta = \frac{\left(\alpha^3 - 2\alpha\right)}{4\left(\alpha^2 - 1\right)}, \tag{4}$$

and

$$A = \left(\frac{\alpha^2}{2} - \alpha\beta\right). \tag{5}$$

Now, screened pseudopotential can be calculated through the relation $v_{ion}(q) = \frac{\omega(q)}{\varepsilon(q)}$, where $\varepsilon(q)$ is the modified Lindhard function $v_{ion}(q)$ is related to Hartree dielectric function, and exchange and correlation function which accounts exchange and correlation interactions for the free electron gas This in turn is used to evaluate second order correction to cold energy (E_{bs}) and hence 0–K total energy E_C (see Ref [27] for more details). Because main objective is to obtain thermodynamic properties of Al at high (finite) temperatures ($T > \theta_D$), ionic motion can be treated classically Under mean-field approximation, vibrational free energy of the lattice ion can be written as

$$F_{ion}(\Omega,T) = -k_B T \left[\frac{3}{2}\ln\left(\frac{mk_B T}{2\pi\hbar^2}\right) + \ln\left\{v_f(\Omega,T)\right\}\right], \tag{6}$$

where

$$v_f(\Omega,T) = 4\pi\int \exp\left[\frac{-g(r,\Omega)}{k_B T}\right] r^2 dr. \tag{7}$$

Here, m is the mass of the ion and $g(r,\Omega)$ in eq. (7) is referred to as the mean-field potential (MFP). The central issue in mean-field theory is the calculation of the MFP $g(r,\Omega)$ Following Wang and Li [2], the MFP in terms of the E_C (cold static energy) is written as follows :

$$g(r,\Omega) = \frac{1}{2}\left[E_C(R_0 + r) + E_C(R_0 - r) - 2E_C(R_0)\right]$$

$$+\left(\frac{\lambda}{2}\right)\left(\frac{r}{R_0}\right)\left[E_C(R_0 + r) - E_C(R_0 - r)\right], \tag{8}$$

where r is the distance that the lattice ion deviates from its equilibrium position, R_0 is the lattice constant with respect to Ω and λ is an integer. The three commonly used expressions for the Grüneisen parameter, *i.e* that due to Slater [28], Dugdale and MacDonald [29], and that for the free volume theory [18], can all be explicitly deduced on the common physical basis corresponding to three different choices for λ, *i.e* −1, 0 and +1, respectively (see Ref. [2] for more details)

The last term in eq. (1) is the Helmholtz free energy due to thermal excitation of free electron gas, which can be written as [30,31]

$$F_{eg} = E_{eg} - TS_{eg}, \tag{9}$$

where E_{eg} is the free electron kinetic, exchange and correlation energies, which have already been included in E_C (see first term of eq. (2)). The entropy contribution S_{eg} is given by,

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3. Calculations

The 0–K total energy $E_C(\Omega)$ in eq (2) is calculated using the local pseudopotential due to Fiolhais *et al* [24]. They have defined two sets of pseudopotential parameters (α and R) so called 'universal' and 'individual' ones Recognizing the importance of the number of valence electrons in the interstitial region between the polyhedral surface of the Wigner-Seitz cell of a monatomic crystal and the surface of the largest inscribed sphere (N_{ins}), they have determined universal set of parameters at zero-pressure condition and assuming N_{ins} to be its uniform-electron-gas value. While the individual ones are, although, derived in the same way and have fitted to an actual value of N_{ins} for each metal, largely to this reason, computed bulk equilibrium properties with this set of parameters were found better than universal ones In this work, we have tried both the versions of the potential parameters and found that 'individual ones' are good working parameters for thermodynamic studies at high temperatures and pressures for Al. The second important point is the choice of λ in eq (8). Wang and Li [2], and Li and Wang [32] found that P-Ω curve do not differ much for different choices of λ. A similar result had also been obtained by Moriarty [33]. Wang and Li [2] have used $\lambda = -1$ for Al, for better thermal expansion at ambient pressure. We have tried all three choices of λ (−1, 0, +1) to compute 300 K equilibrium properties and found that except total energy $F(\Omega,T)$, bulk modulus and volume-thermal expansion differ noticeably from one another (see Table 1) In fact, it is found that the effect of λ on volume-thermal expansion is strong. Inspection of Table 1 reveals that $\lambda = -1$ gives overall good cohesive properties of which volume-thermal expansion is the most influenced one.

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Table. 1 Presently calculated equilibrium properties are tabulated along with the experimental values at 300 K with zero-pressure condition (Experimental cohesive energy is at $T = 0$ K). Experimental cohesive energy and lattice constant are from Ref. [39], bulk modulus is from Ref. [40], and volume-thermal expansion is from Ref. [41].

		Total energy (Ry)	R_0 (a.u.)	B_T (GPa)	β_P (10^{-5} K^{-1})
	−1	−0.2830053	7.781	73.167	5.85
Present calculation	0	−0.2829898	7.772	74.531	4.74
	+1	−0.2829796	7.760	76.520	3.11
Experimental		−0.2492	7.65	72.2	6.93

3.1 Volume-thermal expansion and isothermal bulk modulus

By calculating Helmholtz free energy $F(\Omega,T)$ using eq. (1) as an explicit function of atomic volume Ω and temperature T, one can easily determine the equilibrium volume at a given temperature T by solving $\partial F/\partial\Omega = 0$. With equilibrium $\Omega(T)$ in hand, the volume-thermal expansion coefficient β_P can be calculated as

$$\beta_P(\Omega,T) = \frac{1}{\Omega}\left(\frac{\partial\Omega(T)}{\partial T}\right)_P \tag{11}$$

The isothermal bulk modulus can be calculated by

$$B_T(\Omega,T) = \Omega\left(\frac{\partial^2 F(\Omega,T)}{\partial\Omega^2}\right)_V \tag{12}$$

3.2 Enthalpy, specific heats (C_P and C_V), adiabatic bulk modulus (B_S) and thermodynamic Gruneisen parameter (γ_{th})

The internal energy (enthalpy) at zero pressure can be written as

$$E_H(\Omega,T) = E_C(\Omega) + \xi(\Omega,T)k_BT, \tag{13}$$

where

$$\xi(\Omega,T) = \frac{3}{2} + \left(\frac{\partial \ln \nu_f(\Omega,T)}{\partial \ln T}\right)_V. \tag{14}$$

With $\xi(\Omega,T)$, the specific heat (heat capacity) due to the lattice ion at constant volume is given as

$$C_V^{ion} = k_B\left[\xi(\Omega,T) + T\left(\frac{\partial\xi(\Omega,T)}{\partial T}\right)_V\right] \tag{15}$$

The total constant volume heat capacity C_V can be calculated by using the relation

$$C_V(\Omega,T) = -T\left(\frac{\partial^2 F(\Omega,T)}{\partial T^2}\right)_V \tag{16}$$

The constant pressure heat capacity C_P can be found as

$$C_P(\Omega,T) = C_V(\Omega,T) + \Omega T B_T(\Omega,T)\beta^2(\Omega,T). \tag{17}$$

The adiabatic bulk modulus (B_S) is calculated as

$$B_S(\Omega,T) = B_T(\Omega,T)\left[1 + \frac{T\Omega\beta^2(\Omega,T)B_T(\Omega,T)}{C_V(\Omega,T)}\right] \tag{18}$$

With the isothermal bulk modulus (B_T), the volume-thermal expansion coefficient (β_P) and specific heat at constant volume (C_V), one can calculate the thermodynamic Gruneisen parameter as

$$\gamma_{th}(\Omega,T) = \frac{\Omega B_T(\Omega,T)\beta(\Omega,T)}{C_V(\Omega,T)} \tag{19}$$

3.3 Static equation of state and shock Hugoniot

The relationship of pressure-volume-temperature (P, Ω, T) is called the equation of state (EOS), of which P-Ω relation at constant temperature or simply the isotherm is the most widely studied EOS. At an ambient temperature (T = 300 K), it is obtained through the equation $P = -[\partial F(\Omega,T)/\partial\Omega]$ at constant temperature.

Shock-wave dynamic compression is a common way to study the thermodynamic properties of a substance under extreme conditions such as high-temperature and high-pressure. From derived Hugoniot-state one can deduce much useful information such as EOS at feasible temperature range. The shock Hugoniot in solid state can be obtained with the Rankine-Hugoniot conservation equation [34],

$$P_H(\Omega_0 - \Omega_H) = (E_H - E_0), \tag{20}$$

where Ω_0 and E_0 refer to the atomic volume and energy at ambient conditions, respectively. Solving eq. (20), one can easily derive the Hugoniot volume (Ω_H) *versus* pressure (P_H) as a function of known Hugoniot energy (E_H).

3.4. Melting curve

The determination of the melting curves of materials has

great scientific and technological interest, especially in geophysics and astrophysics. However, obtaining such melting curves remains a major challenge to both experimentalist and theorist, and completely satisfactory explanation of this dynamical phenomenon is yet unresolved Wang *et al* [35] have proposed, considering melting as a process occurring homogeneously throughout the crystal, the one identical to Lindemann law, a relatively simple way to compute high-pressure melting, which can be expressed as

$$T_m = CR_0^2 \left| \frac{\partial^2 F(\Omega, T_m)}{\partial R_0^2} \right| \tag{21}$$

where T_m is the melting temperature and C is a constant for a given element at a given phase before melting For a simple metal, such as Al where no solid-solid phase transitions from the zero-pressure melting point to the pressure studied is known [36,37], constant C can be determined from a fit to the experimental normal melting point Once the constant C is determined, the melting curve can be computed self-consistently from eq (21)

4. Results and discussion

Figure 1 shows a plot of presently calculated curve of cold energy E_C as a function of the fcc-lattice constant along with the theoretical results of Wang and Li [2], and Boettger and Trickey [38] (for fcc-phase) Wang and Li [2], and Boettger and Trickey [38] have used first principles methods, namely FP-LAPW within GGA and full-potential linear combination of Gaussian-type orbitals-fitting function (LCGTO-FF), respectively to evaluate E_C. We have employed local pseudopotential due to Fiolhais *et al* (with individual set of parameters $\alpha = 3\,572$ and $R = 0.317$ a u.), instead. Our calculated 0 K lattice constant is 7.736 a.u , which is about 1 1% higher than that of the experimental value (7.65 a u.) [39] Further, the use of local pseudopotential to evaluate E_C is justified, as calculated bulk modulus (79 7695 GPa) and its pressure derivative (4 25) are in good accord with the experimental values [40], 79.4 GPa and 4 7, respectively. To examine the effect λ, we have calculated equilibrium properties at an ambient condition (see Table 1) with different choices of λ Table 1 clearly demonstrates that the choice of $\lambda = -1$, as pointed out by Wang and Li [2], and also by Moriarty [33], gives overall good results In particular, volume-thermal expansion (β_P) is better in comparison with the other choices of λ Closer inspection of Table 1 manifests that for $\lambda = -1 \rightarrow +1$ bulk modulus increases evidently volume-thermal expansion decreases, since it is a fact that their product (*i e* $B_T \beta_P$) remains nearly constant for most of the simple metals.

Relative volume-thermal expansion (Ω/Ω_0) as a function of temperature at zero-pressure is shown in Figure 2, along with the experimental data [41] and corresponding results of Wang and Li [2] The agreement with the experimental

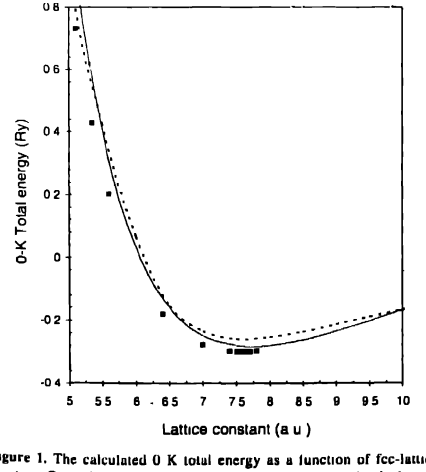

Figure 1. The calculated 0 K total energy as a function of fcc-lattice constant Our calculated results (solid line), the theoretical calculations of Wang and Li [2] (broken line) and those due to Boettger and Trickey [38] (solid squares)

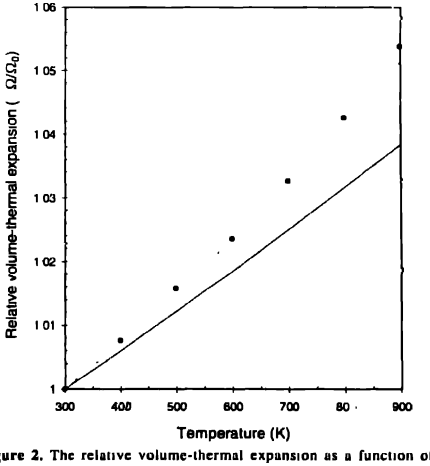

Figure 2. The relative volume-thermal expansion as a function of temperature (solid line), the theoretical results of Wang and Li [2] (broken line) and experimental values (circles) due to Touloukian *et al* [41]

and the *ab initio* results is reasonable, with maximum deviation at highest temperature studied is about 1 5%. Recently, Debernardi *et al* [42] have studied thermodynamic properties of fcc-Al at high temperatures performing an *ab initio* plane-wave pseudopotential method within qausiharmonic approximation Their results for linear-thermal expansion were in excellent agreement with the experimental findings when the thermal expansion of the unit cell is included, even though electronic free energy was completely ignored. This is in contrast to the observation made by Wang and Li [2], who have stressed an importance of electronic free energy at high temperatures for better estimation of thermal properties, particularly, volume-thermal expansion

As a further test of the present approach to the zero-pressure properties, our calculated isothermal bulk modulus *versus* temperature is compared with the theoretical [2] and experimental values [43] (Figure 3) Our results are in fairly good agreement with the experiment and the maximum deviation is within 11% at T = 900 K for this second order derivative of the energy with respect to the volume. It is interesting to note that results due to Wang and Li undervalue B_T for entire range of temperature, while ours overestimate the same Results (not shown in the figure) due to Debernardi *et al* [42] are again in very good agreement with the experimental results

The calculated 300 K static EOS, which is largely governed by the cold energy curve, is shown in Figure 4 The experimental 300 K isotherm for Al at lower

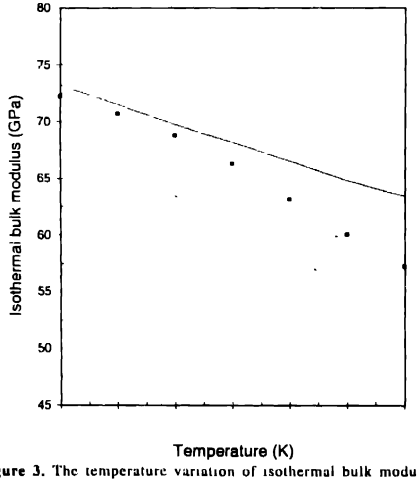

Figure 3. The temperature variation of isothermal bulk modulus (B_T) The present work (continuous line), Wang and Li [2], (broken line) The experimental data (circles) are of Tallon and Wolfenden [43]

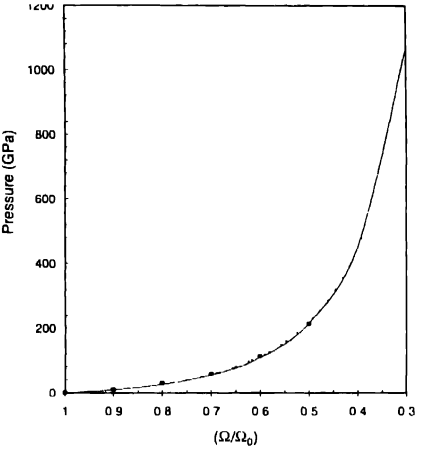

Figure 4 The calculated 300-K isotherm (solid line), measured data (circles) by Greene *et al* [46] and the theoretical results of Wang and Li [2] (broken line)

compressions (not shown in the figure) have been measured by Vaidya and Kennedy [44], and due to Syassen and Holzapfel [45], while experimental points due to Greene *et al* [46] for intermediate range of pressures are compared with the present results Experimentally, the EOS at hundreds of GPa pressures can now be probed even-in static measurements with the diamond anvil cell (DAC) techniques, but extreme pressure (~1 TPa or higher) measurements are still be performed with dynamic, high-temperature shock-wave experiments or alternatively, can be estimated from the first principle methods. In these circumstances, it is worth comparing our results with the *ab initio* results to a pressure range of about 1000 GPa. We have compared our results with corresponding results due to Wang and Li Boettger and Trickey [38] have also obtained T = 300 K EOS using simple analytic form for EOS that was fitted to their first principles results at absolute zero and by adding nuclear-motion contributions. Their results are very much similar to present findings and those due to Wang and Li. Alchagirov *et al* [47] have recently proposed, based on the same structured 'evanescent' local pseudopotential due to Fiolhais *et al* [24], analytic forms for the EOS. These authors have compared their results with the first principles LCGTO-LDA results, and found the level of accuracy that they desired. Presently calculated results when compared with

the *ab initio* findings of Wang and Li agree well for both higher and lower compressions. Maximum deviation of only 6.85% is found at highest pressure. Excellent agreement with the first principles results is consistent with the conclusion drawn by Katsnelson *et al* [25] and Godwal *et al* [26]

The calculated relative enthalpy, from room temperature to melting point, using eq (13) is compared with the experimental [48] and theoretical results due to Wang and Li [2] in Figure 5. The agreement between our computed results, experiment and theory [2] is reasonable with highest departure of 8.94% from experimental value at T = 900 K

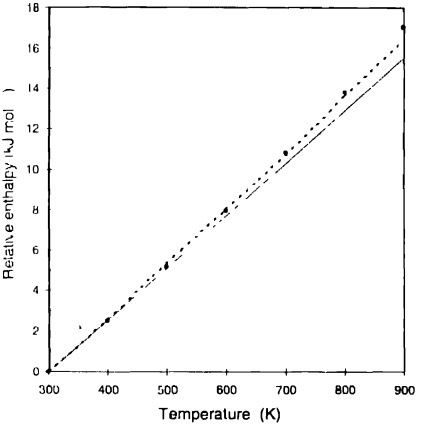

Figure 5. The temperature variation of enthalpy (internal energy) at study (solid line), the theoretical results of Wang and Li [2] (broken line) and experimental data (circles) due to Desai [48]

The calculated C_V^{ion} as a function of temperature is displayed in Figure 6, which is also compared with the experimental values [49] and with the theoretical values of Wang and Li [2]. As expected, C_V^{ion} never exceeds the classical harmonic limit of $3k_B$ (24.94 J mol^{-1} K^{-1}) and somewhat decreases with increasing temperature. This observation is similar to those of Wang and Li [2], and Moriarty [33]. Though, rapid decrease in C_V^{ion} near melting point cannot be observed in the present scheme, nor markedly so with the *ab initio* calculation of Wang and Li. In the present calculation, maximum deviation at melting temperature is found to be 5.33%, which is of the same order of magnitude as the first principles results of Wang and Li. The so-called anharmonic term C_V^{ion-an} may be extracted from C_V^{ion} as $C_V^{ion-an} = C_V^{ion} - 3k_B$. Our calculated results for C_V^{ion-an} are found to be negative for entire range of the temperature and is in agreement with the experimental results [47] and theoretical results of Wang and Li [2], and Moriarty [33]. Moriarty has calculated C_V^{ion-an} up to melting point at an ambient pressure for elemental molybdenum (Mo).

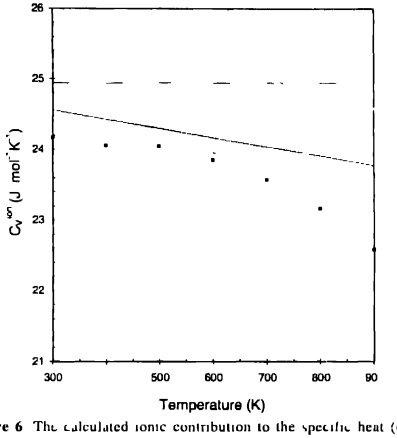

Figure 6. The calculated ionic contribution to the specific heat (C_V^{ion}) *versus* temperature (solid line), the theoretical results due to Wang and Li [2] (broken line) and experimental data [49] (circles). The horizontal dashed line shows the classical harmonic limit to the C_V^{ion}

The calculated temperature variation of C_P and C_V are shown in Figure 7 along with the experimental results of Touloukian [50] for C_P. The experimental values of C_V are

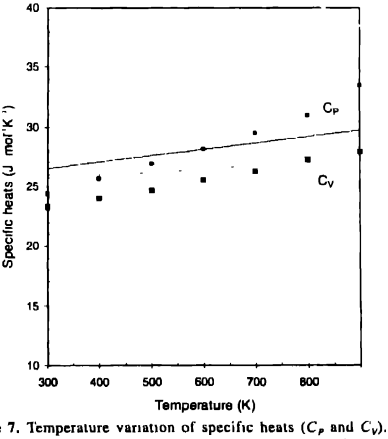

Figure 7. Temperature variation of specific heats (C_P and C_V). The solid lines refer to our calculated results. The experimental results for C_P are taken from Ref. [50] (solid circles) and that for C_V (solid squares) are calculated using eq. (17).

calculated using eq (17). Results due to Debernardi *et al* [42] for these caloric properties were in excellent agreement with the experiments. Variation of C_P, in particular, is less satisfactory in present calculation Upward trend in C_P near melting temperature can not be reproduced Another discrepancy observed is at low temperature (not shown in the figure) For Al, characteristic Debye temperature θ_D is 428 K, below which quantum effects have a role to play. Since the MFP approach treat ionic motion classically, lower temperature regime cannot be evaluated properly Possible source of error in calculated values of C_P at high temperatures lies in inferior estimation of volume-thermal expansion, since expression for C_P contains a term (β_T^2) (C_V and B_T are in relatively better agreement with experiment). Nevertheless, for the entire range of temperature, C_P is found to be greater than C_V which shows the thermal stability of the crystal up to the melting point

The temperature variation of the adiabatic bulk modulus is displayed in Figure 8 The agreement between our theory and experiment (calculated using eq (18)) is very good and maximum deviation is 4 48%

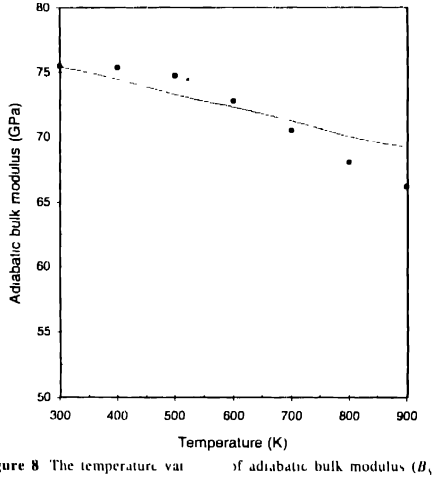

Figure 8 The temperature variation of adiabatic bulk modulus (B_S) (solid line) The experimental results (solid circles) are calculated using eq (18)

The temperature variation of the Grüneisen parameter (γ_{th}) is plotted in Figure 9 Presently calculated Grüneisen parameter is underestimated for the entire range of temperature in comparison with experiment [51] as well as the theoretical results of MacDonald and MacDonald [12]. In our opinion, this is also due to coarse estimation of volume-thermal expansion But weak temperature dependence is in confirmation of those obtained by MacDonald and MacDonald [12]

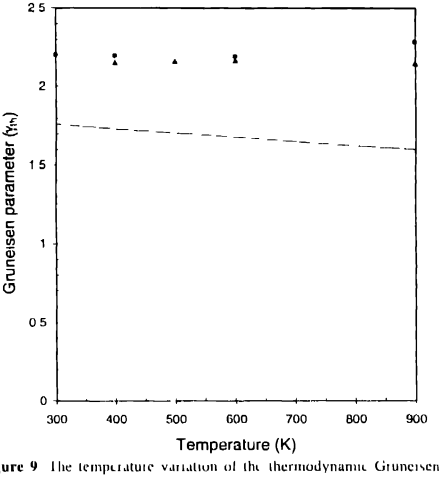

Figure 9 The temperature variation of the thermodynamic Grüneisen parameter (γ_{th}) The presently computed results (solid line) the experimental values [51] (filled circles) and the theoretical estimates (solid triangles) of Ref [12] Broken line is the view to eye

The calculated curve of shock-wave Hugoniot pressure (P_H) *versus* the reduced volume (Ω_H/Ω_0) along with the experimental points from the absolute measurements [52-57] and relative measurements [58,59], and other first principles theoretical results are shown in Figure 10 The absolute measurements are independent of any theoretical model and relative measurements depend on the EOS of reference material Very recently, Chisolm *et al* [37] have elegantly shown that highly accurate EOS for elemental solids can be constructed from decomposition scheme of the total Hamiltonian, essentially, for the nuclei and electrons They found excellent agreement between resulting EOS with the experiments. Our results are agreeably compared with the experimental data and other theoretical findings, which strongly supports the validity of the Rankine-Hugoniot equation and assertion that the shock process can generate a nearly hydrostatic high-pressure state It is to be recalled that in our approach, we have employed the local pseudopotential method to calculate E_C, and both cold and thermal parts of Helmholtz free energy are derived from E_C.

Temperature along shock Hugoniot will be in the range of few hundreds to thousands of degree Kelvin. Thus, the study of shock Hugoniot can be used as benchmark to

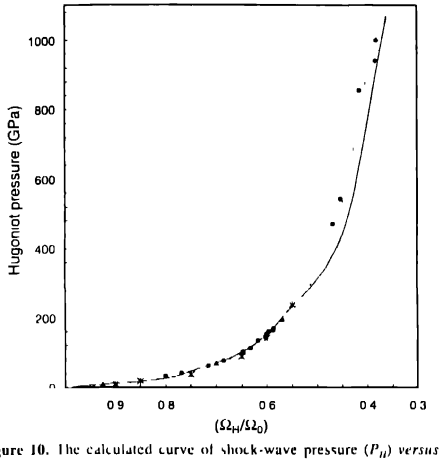

Figure 10. The calculated curve of shock-wave pressure (P_H) *versus* the reduced volume (Ω_H/Ω_0) (solid line) along with the theoretical estimates of Wang and Li [2] (broken line), due to Chisolm *et al* [37] (dotted line) and that due to Godwal *et al* [60] (crosses). Experimental points : solid circles [53], solid triangles [54] and solid diamonds [56].

test the legitimacy and trustworthiness of the theoretical models. Temperature along principal Hugoniot (see Figure 11) is compared with other theoretical estimates [2,37,60]. Except at intermediate reduced volume range, $T_H \rightarrow (\Omega_H/\Omega_0)$ curve is in conformity with the other estimates.

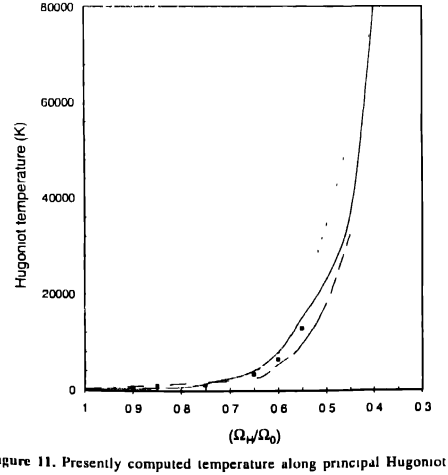

Figure 11. Presently computed temperature along principal Hugoniot (solid line), Wang and Li [2] (broken line), due to Chisolm *et al* [37] (long-dashed line), and Godwal *et al* [60] (solid circles).

As a part of exploring possibilities and reliabilities of using local pseudopotential in conjunction with the MFP approach, we have estimated the most debatable and yet not entirely understood dynamical phenomena, the melting curve. Results are compared with the experimental [61–63] and other first principles theoretical consequences [36,37], and are depicted in Figure 12. Results above pressure of 25 GPa are inferior compare to other findings, though a characteristic nature for fcc-melting curve can qualitatively be obtained. Observed discrepancies may be attributed to the exclusion of the contributions from surface phenomena, vacancies and defects, which are believed to be vital in evaluating high-pressure melting.

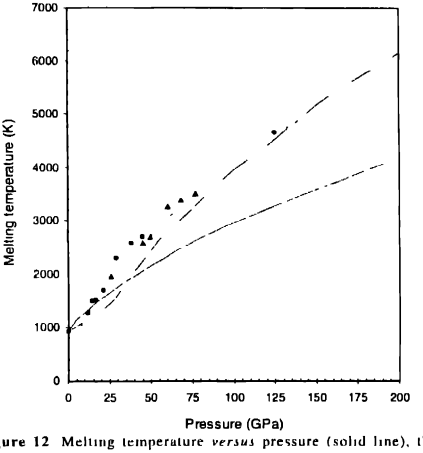

Figure 12. Melting temperature *versus* pressure (solid line), the experimental data, (solid triangles) [61], solid circles [62] and solid diamond [63]. Theoretical results : Alfe *et al* [36] (broken line) and Chisolm *et al* [37] (long-dashed line).

5. Summary and conclusions

In summary, by means of the MFP approach in conjunction with local pseudopotential, we have calculated several thermodynamic properties of elemental Al at high temperatures and pressures. The MFP seen by the lattice ion is constructed in terms of the cold energy E_C, which in the present paper is evaluated, alternatively, using local pseudopotential due to Fiolhais *et al* [24]. Overall good agreement for properties that we calculate is obtained, except for caloric properties, thermodynamic Grüneisen parameter and melting curve. The discrepancies observed, in particular, for specific heats at high temperatures, in our opinion are due to inferior estimation of volume-thermal expansion at zero-pressure. Volume-thermal expansion is quite sensitive to the microscopic dynamical quantities

such as phonon frequencies, mode Grüneisen parameter and concavity parameter, where latter describes the deviation from the linear behavior of the volume dependence of the phonon frequencies Pollack *et al* [64] have shown that calculated phonon frequencies with the same local pseudopotential are too high in symmetric directions for Al Thus, possible improvement can be achieved, if pseudopotential parameters have been determined by fitting phonon frequencies as well

In contrast, high-pressure properties such as static EOS, shock Hugoniot and temperature along principal Hugoniot, are in excellent agreement with the experiments and other first principles results It is known that for elemental Al, there is a slight admixture of *d*-electrons near the Fermi surface, an effect that increases as the volume decreases In fact, some of the *d*-bands cross below the *p*-bands in some region of the Brillouin-zone including the region of the Γ-point [65] It seems that such a hybridization effect is accounted properly in the present study at high-pressure

On the encouraging side, the present scheme enjoys an advantage of computational simplicity compared to the first principles methods Even in conventional pseudopotential formalism, to obtain Helmholtz free energy at an equilibrium volume, one needs to evaluate phonon frequencies at large number of wave vectors in Brillouin-zone and phonon density of states at each volume for a given temperature, which by no means is favorable mathematically On the contrary, present scheme completely bypasses these cumbersome computations, and total Helmholtz free energy can be obtained by evaluating only one-dimensional numerical integration once the 0 K total energy is obtained using local pseudopotential Thus, we conclude that the use of local pseudopotential in conjunction with the MFP method in condensed matter physics is a good operational proxy, owing to its computational simplicity and consistency The presently calculated results confirm that the pseudopotential due to Fiolhais *et al* [24], which is controlled by three dominant parameters namely, the electron density, the valence *Z* and the density on the surface of the Wigner-Seitz cell, developed within the condensed state environment is found to be transferable to the other thermodynamic states (*i.e.* high-temperature and high-pressure states) without changing the values of the parameters. This transferability has been checked successfully in the case of liquid alkali metals [66,67] and liquid alkaline-earth metals [68] using molecular dynamics (MD) method.

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